Polaron Contribution to the Infrared Optical Response of $La_{2-x}Sr_xCuO_{4+\delta}$ and $La_{2-x}Sr_xNiO_{4+\delta}$

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The anomalous midinfrared absorption band in the optical conductivity of $La_{2-x}Sr_xCuO_{4+\delta}$ $La_{2-x}Sr_xNiO_{4+\delta}$ is interpreted in terms of photon-assisted hopping of small polarons. An analysis of the normal-state single crystal a-b plane data indicates that polarons in $La_{2-x}Sr_xNiO_{4+\delta}$ are small, whereas in $La_{2-x}Sr_xCuO_{4+\delta}$ the polarons are larger. The absence of bulk superconductivity in $La_{2-x}Sr_xNiO_{4+\delta}$ may be linked with smaller polaron size.

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Anomalous midinfrared optical absorption, referred to as the "mid-IR band" (MIRB) [1], has been observed in the normal-state optical response of virtually every high-T_c CuO_4-based superconductor. A broad band is found in the a-b plane $\sigma_1(E)$ with a band maximum E_m in the range $0.1 < E_m < 0.5$ eV, depending on the material [2-4]. The importance of understanding the origin of this band is underscored by the early observations that T_c correlates with the MIRB oscillator strength in $La_{2-x}Sr_xCuO_{4+\delta}$ (LCO) [5,6]. In a previous paper [7], we reported the existence of a MIRB in $La_{1.8}Sr_{0.2}NiO_{4+\delta}$, which is isostructural to $La_{1.8}Sr_{0.2}CuO_{4+\delta}$. This result is interesting because $La_{2-x}Sr_xNiO_{4+\delta}$ (LNO) does not exhibit bulk superconductivity. In this Letter, we report the results of our Sr-doping study of the MIRB in LNO from which we find that the Sr dependence of the MIRB strength in the LNO is identical to that reported for LCO [5,6]. Second, we report the results of a quantitative study of the frequency dependence of the MIRB contribution to the optical conductivity in LNO. We find that $\sigma_1(E)$ from $E \sim 0$ up to the band maximum is well fitted by small polaron theory. Since the Sr dependence of the MIRB strength in the LNO and LCO are identical, we then argue that polarons are responsible for the MIRB in the LCO as well. Third, we find that the polaron size is larger in LCO than in LNO, which may be an important key in understanding the superconducting pairing mechanism in high-T_c materials and explain why the LNO does not exhibit bulk superconductivity.

Several key theoretical investigations [8-13] of the optical properties of small polarons have been presented since the pioneering paper of Holstein [14]. The first theoretical discussion of superconductivity through bipolaron formation in transition metal oxides was provided by Chakraverty [15] and motivated Bednorz and Muller [16] to search for high-T_c superconductivity in these materials. Soon after the discovery of the high-T_c oxide superconductors, polaron-related theoretical models were proposed by several authors to explain the observed high transition temperatures [17-19]. To date, it appears that no agreement has been reached on the role of polarons in the high-T_c oxides. On the experimental side, small polarons have been identified by Mihailovic *et al.* [20] with a photoinduced MIRB in the insulating parent compounds of high-T_c oxides.

LNO is an interesting isostructural counterpart to LCO which, however, does not exhibit bulk superconductivity, although anomalous dimagnetism has been reported below $T = 70$ K in undoped and Sr-doped samples [21]. Both LNO ($T_N = 650$ K) and LCO ($T_N = 290$ K) exhibit similar magnetic properties [22], photon dispersion [23], and structural transitions albeit at different temperatures [22]. In contrast to LCO, LNO exhibits almost no contribution to the IR σ_1 from bandlike carriers, which allows the MIRB to be investigated without interference from an itinerant carrier background.

In Fig. 1, we display $\sigma_1(E, T = 300$ K) data (dashed lines) for several single crystals of LNO with $(x,\delta) = (0.00,0.00)$, $(0.05,0.00)$, $(0.10,0.00)$, $(0.00,0.085)$, and $(0.20,0.00)$ over the photon energy range $0 < E < 1$ eV. A description of the Kramers-Kronig transformation necessary to extract σ_1 from R collected over the range 0-6 eV has been provided earlier [7]. σ_1 exhibits sharp structure at the lowest energies which arises from TO phonons. The broad band with a maximum near 0.5 eV is identified with anomalous MIR absorption, and is similar to the a-b plane response reported in LCO single crystals by Uchida *et al.* [3] and polycrystalline samples by Orenstein *et al.* [5]. In insulating $La_2NiO_{4+\delta}$ ($\delta \sim 0.00$), no MIRB is observed [7]. Furthermore, an oxygen-doped, Sr-free sample ($x = 0.0$, $\delta = 0.085$) was found to exhibit a similar MIRB, indicating this band is not associated with transitions involving Sr states.

The solid lines in Fig. 1 are calculated using an approximate result derived for photon-assisted hopping of small polarons between next-neighbor sites distributed with cubic symmetry which is given by [11-13]

$$\sigma_{1H}(E,T) = zNe^2a_0^2\frac{\sqrt{\pi}}{6h}\frac{J^2}{kT(2E_bkT)^{1/2}}e^{-E_b/2kT}\frac{\sinh(E/2kT)}{E/2kT}\exp(-E^2/8E_bkT), \quad kT \geq \frac{1}{2}\hbar\omega_0, \tag{1}$$

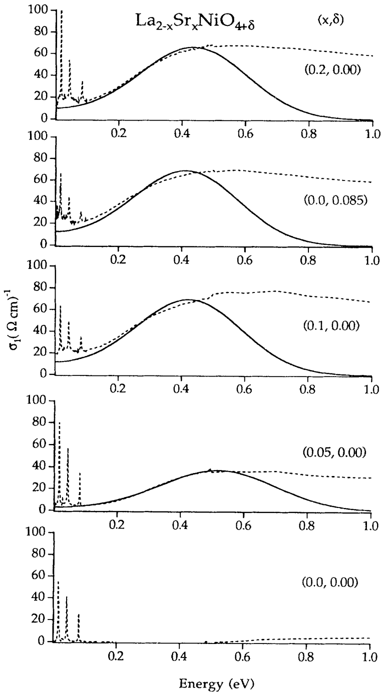

FIG. 1. Optical conductivity (dashed lines) of $La_{2-x}Sr_xNiO_{4+\delta}$ ($T=300$ K). Solid curves are calculated according to Eq. (1).

where E_b and J are, respectively, the polaron binding energy and electronic transfer integral between nearest-neighbor sites, ω_0 is the average frequency of the phonon cloud associated with a small polaron, a_0 is the lattice constant, z is the site coordination number, and N is the polaron density. Equation (1) describes a band with a maximum at $E=E_m=2E_b$. A similar form to Eq. (1) has been used, for example, by Muhlstroh and Reik [24] to study polarons in isotropic Sr-doped $LaCoO_3$. Despite the anisotropy in TiO_2, Bogomolov *et al.* [8,25] have used Eq. (1) to extract the small polaron parameters for this material. In both cases, these authors found that the dc conductivity $\sigma_{1H}(0,T)$ [$E=0$, Eq. (1)] is in reasonable agreement with the $\rho(T)$.

At $T=300$ K, $2kT \gtrsim \hbar\omega_0$ is satisfied for $La_2CuO_{4+\delta}$, where $\hbar\omega_0 \sim 0.05$ eV [20], and this condition should also be satisfied for $La_2NiO_{4+\delta}$ since it exhibits similar phonon dispersion [23]. The values for the $\sigma_{1H}(0,300\text{ K})$ and E_b resulting from the analysis of the LNO data in Fig. 1 are listed in Table I together with results of other small polaron materials such as $TiO_{2-\delta}$ [8] and La(Sr)CoO_3 [24]. Also included in the table are values of the small polaron parameter $\eta=2E_b/\hbar\omega_0$, which is a measure of the magnitude of the electron-phonon coupling strength [13]. It can be seen that the values $E_b \sim 0.24$ eV and $\eta \sim 10$ for the LNO are typical of small polaron materials: TiO_2 ($E_b \sim 0.4$ eV, $\eta \sim 8$) [8,25] and $LaCoO_3$ ($E_b \sim 0.35$ eV, $\eta \sim 9$) [24]. From experimental values of $E_m=2E_b$ and $\sigma_{1H}(E_m)$, we can estimate J for the LNO using Eq. (1). To minimize complications arising from possible polaron-polaron correlation expected to occur for large x, we use the results from the $x=0.05$ sample. The polaron density $\sim 5.3\times 10^{20}$ cm^{-3} is calculated assuming one polaron for every Sr atom introduced in the lattice and using a cell volume $V=95$ Å^3 for each Ni site [26]. Using $a_0=V^{1/3}=4.6$ Å, $z=6$, $\sigma_{1H}(E_m)\sim 40$ Ω^{-1}cm^{-1}, and $E_b=0.29$ eV in Eq. (1), we obtain $J_{Ni} \sim 0.08$ eV, comparable to that of TiO_2($J\sim 0.1$ eV [8]) and smaller than that of doped $LaCoO_3$($J \sim 0.2$ eV [24]). To make contact with available transport studies on the LNO, we find $\sigma_{1H}(0,300\text{ K}) \sim 10$ Ω^{-1}cm^{-1} for $La_{1.8}Sr_{0.2}NiO_4$ (Table I), in good agreement with the experimental dc conductivity $\sigma_{dc} \sim 15$ Ω^{-1}cm^{-1} [27].

The lack of agreement in $\sigma_1(E)$ between theory and experiment for $E > E_m$ apparent in Fig. 1 has also been noted for the classic small polaron material TiO_2. Several mechanisms have been proposed to explain this difference [12], including photon-assisted hopping to second and more distant sites. In the case of LNO, the low energy onset of interband transitions at $E \sim 0.5$ eV (Fig. 1) may also contribute to the experimental conductivity for $E \gtrsim E_m$ and contribute to the difference in the calculated and observed σ_1. Furthermore, at high polaron concentrations (i.e., $x \gtrsim 0.1$), correlation effects may also lead to a distortion of the MIRB.

From Eq. (1), $\sigma_{dc} \sim T^{-3/2}\exp(-E_b/2kT)$, consistent with a T-activated conductivity (i.e., the activation energy E_a is one-half the polaron binding energy [28]). From

TABLE I. Polaron parameters for $La_{2-x}Sr_xNiO_{4+\delta}$, $La_{2-x}Sr_xCuO_{4+\delta}$, $TiO_{2-\delta}$ [12], La(Sr)CoO_3 [24], and $SrTiO_{3-\delta}$ [30].

	$La_{2-x}Sr_xNiO_{4+\delta}$				$La_{2-x}Sr_xCuO_{4+\delta}$				$TiO_{2-\delta}$ [12]	La(Sr)CoO_3 [24]	$SrTiO_{3-\delta}$ [30]
J (eV)	0.08				0.2				0.1	0.215	0.25
$\hbar\omega_0$ (eV)	0.05				0.05				0.1	0.078	0.085
x	0.05	0.10	0.17[a]	0.20	0.02	0.06	0.10	0.15			
E_b (eV)	0.29	0.24	0.24	0.25	0.30	0.22	0.12	0.06	0.4	0.35[b]	0.23[b]
η ($2E_b/\hbar\omega_0$)	11.6	9.6	9.6	10.0	12.0	8.8	4.8	2.4	8	9	5.4
ξ ($J/\eta\hbar\omega_0$)	0.14	0.16	0.16	0.16	0.33	0.45	0.83	1.7	0.12	0.31	0.54
σ_{1H} $(\Omega\,cm)^{-1}$	3.0	11.6	12.4	10.1							

[a]Oxygen doped ($x=2\delta$).
[b]Calculated from values of η and $\hbar\omega_0$.

the optical data for $La_{1.8}Sr_{0.2}NiO_4$ we obtain $E_b=0.25$ eV or $E_a^{opt}=0.12$ eV (Table I), larger than the transport value $E_a^{tr}\sim0.03$–0.05 eV [27]. However, the difference between E_a^{opt} and E_a^{tr} has been discussed by Reik [13] and Austin [28], and observed, for example, in TiO_2 ($E_a^{opt}\sim0.2$ eV and $E_a^{tr}\sim0.15$ eV) [8,25], V_2O_5 ($E_a^{opt}\sim0.22$ eV and $E_a^{tr}\sim0.17$ eV) [29], and $SrTiO_3$ [30] where $E_a^{opt}\sim0.06$ eV, yet the σ_{dc} does not exhibit activated behavior.

In Fig. 2, we plot the Sr dependence of the normalized MIRB strength for single crystal LNO, LCO [3], and polycrystalline LCO [5]. The data point for $La_2NiO_{4.085}$ is included in Fig. 2 by assuming that an oxygen excess $\delta=0.085$ contributes the same number of polaronic holes in the a-b plane as supplied by a Sr doping of $x=0.17$. The solid curve in the figure represents a guide to the eye and is given by $f(x)=(x-x_0)[1-c(x-x_0)]$, where $c=4.5$ and $x_0=0.04$. *The nearly identical Sr dependence of the MIRB strength in LCO and LNO is evident, indicating that the MIRB in these two materials stems from the same mechanism.* Consistent with our interpretation of the optical data for LNO, we suggest that this common mechanism is the optical response of small polarons. To make contact with previous work on polycrystalline LCO by Orenstein *et al.* [5] and by Etemad *et al.* [6] that first pointed out the correlation of T_c and MIRB strength, we include their data in Fig. 2.

From σ_1 data of Uchida *et al.* [3] for LCO, we can also obtain using Eq. (1) values for the polaron parameters E_b and J. Considering their data for semiconducting $La_{1.94}Sr_{0.06}CuO_4$, where the MIRB maximum does not overlap a broad, underlying Drude-like background, we obtain estimates for $J_{Cu}=0.2$ eV and $E_b=0.23$ eV, for $E_m=0.45$ eV and $\sigma_{1H}(E_m)\sim370\ \Omega^{-1}cm^{-1}$ estimated from Fig. 7 in Ref. [3], $z=6$, $V=95$ Å^3 [31], $a_0=V^{1/3}$, and $N=6.3\times10^{20}$ cm^{-3}. As a result of these estimates, we see that $J_{Cu}\sim2.5J_{Ni}$, signaling that the electron transfer between next-neighbor Cu sites is much easier than between next-neighbor Ni sites.

In Fig. 3, we display the a-b plane σ_1 of Uchida *et al.* (solid circles, $T=300$ K) for $La_{1.9}Sr_{0.1}CuO_4$ ($T_c=18$ K) [3]. The error bars indicate our uncertainty in digitizing their data for $E<0.08$ eV. It is clear that a second broad contribution, in addition to a MIRB, is present in their data. As is common in the analysis of high-T_c optical data [1], we fit this contribution with a Drude-like background $\sigma_{1D}(E)$ (dotted line), and identify this contribution with a second (delocalized) carrier type in the system. The dashed curve represents the contribution from small polarons $\sigma_{1H}(E)$. Thus the total $\sigma_1(E)$ (solid curve) is given by $\sigma_{1D}(E)+\sigma_{1H}(E)$. The Drude term is parametrized by a free carrier relaxation time τ_D and dc conductivity $\sigma_{1D}(0)$, $\sigma_1(E)$ is calculated using $\sigma_{1D}(0)=587\ \Omega^{-1}cm^{-1}$, $\tau_D=1.2\times10^{-13}$ s, $\sigma_{1H}(0)=507\ \Omega^{-1}cm^{-1}$, and $E_b=0.12$ eV. The data in Fig. 3 are reasonably well described by this two-carrier model for $E<E_m$. We interpret the agreement between data and model calculation over this limited energy range as qualitative evidence suggesting the applicability of a two-carrier model for $La_{1.9}Sr_{0.1}CuO_4$ in the normal state. Furthermore, using these parameters we compute a dc resistivity $\rho_{dc}=[\sigma_{1D}(0)+\sigma_{1H}(0)]^{-1}=914\ \mu\Omega$ cm, comparing favorably with the value $\rho_{dc}\sim1000\ \mu\Omega$ cm obtained for the same sample in transport studies [3]. Note that for $T=300$ K the contributions to ρ_{dc} from bandlike and small polaron carriers are almost equal.

A characteristic feature associated with the MIRB in high-T_c oxides is its weak T dependence [1], especially in the energy range $E>E_m$. This region has been proposed

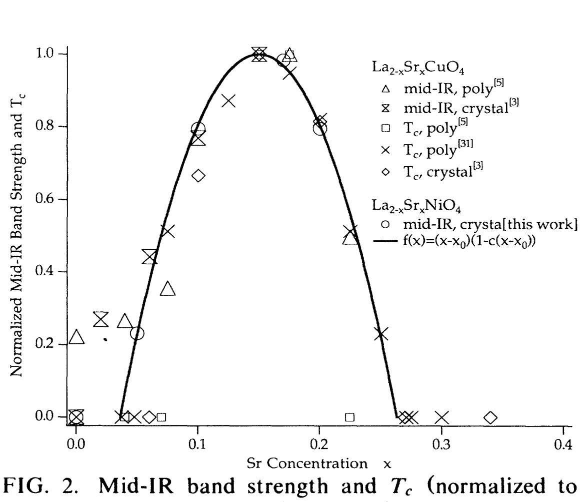

FIG. 2. Mid-IR band strength and T_c (normalized to the respective maximum values) vs Sr(x) concentration for $La_{2-x}Sr_xNiO_{4+\delta}$ and $La_{2-x}Sr_xCuO_{4+\delta}$. The solid line is a guide to the eye. The labels "poly" and "crystal," respectively, refer to polycrystalline and single crystal data.

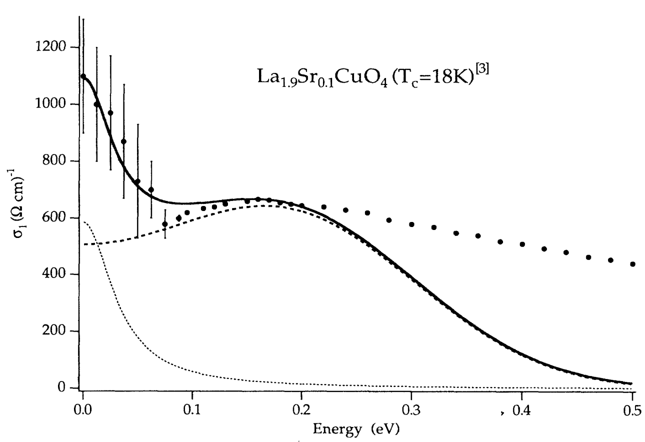

FIG. 3. Optical conductivity $\sigma_1(E)$ for $La_{1.9}Sr_{0.1}CuO_{4+\delta}$ [3]. The solid, dashed, and dotted curves represent the total calculated $\sigma_1(E)$, the polaron contribution to $\sigma_1(E)$ [Eq. (1)], and a Drude-like contribution to $\sigma_1(E)$, respectively. The error bars arise from our uncertainty in digitizing the experimental conductivity of Uchida *et al.* [3] for $E<0.08$ eV.

to contain contributions to σ_1 from photon-assisted hopping to next-neighbor and more distant sites [12]. To our knowledge, the T dependence of photon-assisted hopping to second and higher neighbors has not yet been reported. Reik [3] has considered the T dependence of $\sigma(\omega)$ for next-neighbor hopping in $SrTiO_{3-\delta}$. Using numerical methods, he finds that $\sigma_{1H}(E, 300\ K)$ for $E \gg \hbar\omega_0$ is almost identical to the calculated $T=0$ K result $\sigma_{1H}(E,0)$, indicating a weak T dependence in this photon energy range. Similar to the work of Reik [30], we have calculated using his expressions $T=0$ K $\sigma_1(E)$ of $La_{1.9}Sr_{0.1}CuO_4$ using the parameter values $\eta=2E_b/\hbar\omega_0=4.8$, $\hbar\omega_0=0.05$ eV, which we obtained from the optical analysis of $T=300$ K data (Fig. 3). From this calculation, we find not more than a 15% increase in $\sigma_1(E_m)$ as T decreases from 300 to 0 K, and, for $E > E_m$, this percent difference decreases, consistent with the experimental results [32].

It is interesting to consider the ratio $\xi=J/\eta\hbar\omega_0$ in Table I which is proportional to the polaron size [30]. $\xi < 1$ or $J < \eta\hbar\omega_0$ is necessary for Eq. (1) to be applicable [24]. For example, values for ξ for the classic small polaron materials are $TiO_{2-\delta}(\xi \sim 0.12)$ and $La(Sr)CoO_3(\xi \sim 0.3)$. For LNO we find $\xi \sim 0.16$, indicating the polarons are *small*. However, using our estimates for J and E_b for LCO, we find that the polarons in these superconducting LCO are larger ($\xi > 0.33$). Similar values for ξ have been obtained for *superconducting* $SrTiO_{3-\delta}$ [30] ($T_c=0.3$ K [33]) where $\xi \sim 0.54$. In LCO, ξ increases from 0.33 to 1.7 with increasing x (Table I), tracking the reduction of E_b and a dopant-induced transformation to metallic conductivity. Note that for LCO the polarons tend to be small in the dilute limit (small x), consistent with the report [20] that the photoinduced charge carriers in $La_2CuO_{4+\delta}$ are small polarons with $\eta \sim 10$ (or equivalently $\xi \sim 0.4$). Whereas in the limit of large x, the polarons tend to expand (Table I), and their contribution to $\sigma_1(\omega)$ is overwhelmed by the contribution from bandlike carriers (see Fig. 7 in Ref. [3]). However, ξ is not very sensitive to x in LNO (Table I) and metallic conductivity does not occur until $x \sim 1$ [34-36]. The tendency of LNO to resist a Sr-induced transformation to a metallic state and bulk superconductivity may be linked with the smaller polaron size in the LNO which favors carrier localization [37]. Finally, for LCO, it remains to be understood why increasing Sr induces an expansion of the polaron size (or reduction of the polaron binding energy), and what role this expansion plays in the superconductivity of this system.

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Note added.—At the time of the submission of our manuscript, we were unaware of the paper by T. Ido *et al.* [Phys. Rev. B **44**, 12094 (1991)]. All spectral features reported here have also been observed by Ido *et al.* However, there is a distinct difference concerning the dependence of the MIRB strength on Sr content, which may be connected with oxygen stoichiometry. Our samples had been annealed in a CO/CO_2 mixture as described in Ref. [7] so that $\delta \sim 0$.

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